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SALTS OF GALACTURONIC ACID AND THEIR APPLICATION TO THE PREPARATION OF GALACTURONIC ACID FROM PECTIC SUBSTANCES

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ABSTRACT

Twelve new salts of galacturonic acid have been prepared and their properties investigated. Crystalline sodium, potassium, ammonium, cadmium, and silver galacturonates have been found to contain the beta pyranose modification, and crystalline calcium and strontium galacturonates, the alpha modification. A unique type of double salt containing a monovalent and a divalent metal in combination with the alpha pyranose modification of galacturonic acid has been obtained, and the following members of this class have been crystallized and studied: Sodium calcium, sodium strontium, sodium barium, sodium cadmium, sodium lead, and potassium calcium galacturonates. Mutarotation studies have been conducted in order to determine the structure of the galacturonate component in the salts. The crystallizing properties of the normal calcium and strontium galacturonates, and especially of the sodium calcium and sodium strontium galacturonates, makes these salts particularly suitable for the separation of galacturonic acid from the hydrolytic liquors of plant materials.

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I. PREPARATION OF GALACTURONIC ACID FROM PECTIC SUBSTANCES

Even though galacturonic acid in the form of pectic substances comprises a large part of the carbohydrate material of plants, its properties have not been closely studied nor has its industrial application been explored. The slowness in the development of the chemistry of galacturonic acid has undoubtedly been due to the lack of a convenient method for the separation of the acid from plant material. Heretofore [1]¹ the preparation of galacturonic acid has involved, first, the preparation of pectin or pectic acid from the plant material; second, hydrolysis of the purified pectin or pectic acid; third, alcoholic precipitation of impurities; and finally, crystallization of the galacturonic acid in the form of a monohydrate from the alcoholic extract.² Extraction and crystallization processes involving the use of alcohol are expensive and preclude the production of a low-cost product.

Prior to the present investigation a crystalline sodium salt [8, 9], an amorphous barium [10, 11, 12] and an amorphous calcium [8, 9] salt were reported in the literature, but these compounds are not satisfactory for the separation of galacturonic acid from crude mixtures. Since a slightly soluble salt would provide a means for separating galacturonic acid directly from the hydrolyzates of plant materials, the preparation of a series of salts was undertaken with the object of obtaining a compound that could be used for separating galacturonic acid from the liquor obtained by the partial hydrolysis of such materials as apple pulp, citrus fruit pulp, and beet pulp.

The present investigation was successful in that new crystalline potassium, ammonium, cadmium, silver, calcium, and strontium salts have been obtained, and, in addition, a new type of double salt. The double salts, which appear to be unique in the field of carbohydrate chemistry, contain one atom of a monovalent metal and one of a divalent metal in combination with three galacturonate radicals. As representatives of the class of double compounds, crystalline sodium calcium, sodium strontium, sodium barium, sodium cadmium, sodium lead, and potassium calcium galacturonates have been prepared.³ The double salts, in general, are less soluble than the normal salts and crystallize exceptionally well. For this reason they are useful for separating galacturonic acid from sirups of relatively low purity. Thus it has been found that sirups obtained by the hydrolysis of pectin-containing material, when neutralized with a calcium base yield crystalline calcium galacturonate, or when neutralized with a sodium and a calcium base yield crystalline sodium calcium galacturonate.

The existence of a simple means for obtaining galacturonates from cheap raw materials opens the way for numerous applications in the

¹ Figures in brackets indicate the literature references at the end of the paper.

² Early work on the preparation of galacturonic acid from pectic substances was done by Ehrlich and coworkers, who developed a method that gives high yields of galacturonic acid but requires a pectinase especially prepared from *Penicillium Ehrlichii* [2]. Morrell, Baur, and Link [3] described a method for preparing the acid in quantity from commercially available citrus pectic acid by means of acid hydrolysis. Mottorn and Cole [4] modified the Ehrlich method by using commercially available pectic acid and a commercial pectinase, Pectinol 100D. Pigman [5] improved the procedure further by the use of methyl alcohol as a solvent for extracting the crude galacturonic acid from the hydrolyzate. Later, Isbell and Frush [6] introduced the use of acetic acid as a solvent in the crystallization of galacturonic acid, and Rietz and Maclay [7] pointed out that the modified Ehrlich method is applicable to commercial pectins.

³ After the work described in this paper had been completed and the manuscript written, the preparation of sodium calcium galacturonate and potassium calcium galacturonate was reported in a patent [13] issued, January 4, 1944, to Pasternack and Regna. Our work was conducted without knowledge of that described in the afore-mentioned patent.

chemical industry. Catalytic reduction of the calcium salt with hydrogen in the presence of Raney nickel yields calcium *L*-galactonate, an intermediate in a new process for the manufacture of vitamin C that has been developed by the senior author. Oxidation of the salts in alkaline solution with oxygen yields salts of trihydroxyglutaric acid [14], and electrolytic oxidation in the presence of bromides or oxidation with chlorous acid yields mucic acid [15]. We have observed that the sodium, potassium, and calcium salts inhibit the precipitation of the hydroxides of the amphoteric metals, such as aluminum and chromium. Hence some of the galacturonates may find use in the tanning and dyeing industries. Furthermore, the silver salt in solution decomposes spontaneously with the formation of silver mirrors; hence it might be used for the silvering of glass. The new salts are of academic interest because they are characteristic derivatives of galacturonic acid suitable for identification purposes, and because they provide a convenient raw material for the production of substances having the *L*-galactose configuration.

Directions are given on page 87 for the preparation of calcium galacturonate from citrus pectin, and on page 90 for the preparation of sodium calcium galacturonate from citrus pectic acid. The preparation of the same salts from cheaper raw materials as, for example, the pulp which remains after the extraction of sugar from sugar beets, will be the subject of a future publication.

II. MODIFICATIONS OF GALACTURONIC ACID IN CERTAIN SALTS

Inasmuch as the galacturonate radical can exist in pyranose, furanose, and open-chain modifications, salts of galacturonic acid having the same empirical formula but different structures and configurations are possible. It is therefore of interest to ascertain what modifications exist in the new salts; this may be determined by a study of the optical rotations. In a previous publication [6] it was shown that the two crystalline modifications of galacturonic acid comprise a pair of pyranoses, and that they give complex mutarotations which resemble the mutarotations of α - and β -*D*-galactose.

Measurements have now revealed that the salts of galacturonic acid also exhibit mutarotation. When the salts are dissolved in carbon-dioxide-free water, the changes in optical rotation are too rapid for accurate measurement, and the mutarotation constants vary widely for different salts and for different samples of the same salt. Somewhat more consistent results were obtained from measurements conducted in water saturated with carbon dioxide, but, nevertheless, the variation in the constants for the various salts was too large to permit a satisfactory correlation of optical rotation and structure. In every case the mutarotation of the salt was found to be more rapid than the mutarotation of the free acid.

The more rapid mutarotations of the salts appear to be caused by the catalytic effect of the galacturonate ion. As shown by Lowry [16] and by Brønsted and Guggenheim [17], the mutarotation reaction is accelerated by all substances capable of donating protons, or accepting protons. In an aqueous solution of a sugar the principal catalysts are the undissociated water molecules, hydrogen ions, and hydroxyl ions. Salts of carboxylic acids, such as sodium acetate,

accelerate mutarotation through combination of carboxylate ions with protons. The carboxylate ions derived from salts of galacturonic acid act in similar manner and thereby accelerate the mutarotation. For this reason the mutarotation constants obtained for the salts of galacturonic acid depend in part on the concentration of the salt. Solutions of galacturonic acid contain relatively small concentrations of the carboxylate ion, but the acid affects the rate of mutarotation through the catalytic effect of the hydrogen ions and of the undissociated acid molecules. In dilute aqueous solution the catalytic effect of the acid is less than the catalytic effect of the salt, and consequently the mutarotation of the acid is less rapid than that of the salt.

The correlation of the mutarotations of the salts with those of the alpha and beta modifications of galacturonic acid is complicated by these factors. However, by treating the salts with 1 equivalent of a mineral acid they are converted almost instantaneously into galacturonic acid, and the mutarotation which follows is essentially that of the free acid in the presence of a salt of a strong acid. Inasmuch as salts of strong acids have little effect on the mutarotation rate, the constants obtained for the salts in the presence of an equivalent quantity of acid should be comparable with the constants for galacturonic acid in aqueous solution of like concentration.

Some results obtained by measurement of the mutarotation which follows dissolution of 0.002 equivalent of a salt of galacturonic acid in 25 ml of water containing 0.002 equivalent of nitric acid are summarized in the form of the mutarotation equations reported in table 1.

TABLE 1.—*Optical rotations of salts dissolved in an equivalent quantity of aqueous nitric acid*^a

Substance	Mutarotation equation ^b	Initial rotation ^c
ALPHA PYRANOSE MODIFICATIONS		
α -D-Galacturonic acid ^d	$^{\circ}S = +9.52 \times 10^{-0.0119t} + 2.08 \times 10^{-0.115t} + 10.01$	$^{\circ}S$ +21.61
Calcium galacturonate	$^{\circ}S = +9.39 \times 10^{-0.0144t} + 2.25 \times 10^{-0.105t} + 9.93$	+21.57
Strontium galacturonate	$^{\circ}S = +9.26 \times 10^{-0.0153t} + 2.41 \times 10^{-0.114t} + 10.03$	+21.70
Sodium calcium galacturonate	$^{\circ}S = +9.31 \times 10^{-0.0137t} + 2.52 \times 10^{-0.125t} + 10.02$	+21.85
Sodium strontium galacturonate	$^{\circ}S = +9.25 \times 10^{-0.0148t} + 1.89 \times 10^{-0.145t} + 9.92$	+21.06
Sodium barium galacturonate	$^{\circ}S = +8.63 \times 10^{-0.0147t} + 2.01 \times 10^{-0.112t} + 9.78$	+20.42
Sodium cadmium galacturonate	$^{\circ}S = +8.69 \times 10^{-0.0148t} + 1.99 \times 10^{-0.104t} + 9.87$	+20.55
Sodium lead galacturonate	$^{\circ}S = +9.54 \times 10^{-0.0480t} + 1.68 \times 10^{-0.262t} + 10.01$	+21.23
Potassium calcium galacturonate	$^{\circ}S = +9.52 \times 10^{-0.0154t} + 2.04 \times 10^{-0.126t} + 9.91$	+21.47
BETA PYRANOSE MODIFICATIONS		
β -D-Galacturonic acid ^d	$^{\circ}S = -5.81 \times 10^{-0.0120t} + 0.93 \times 10^{-0.092t} + 9.71$	+4.83
Sodium galacturonate	$^{\circ}S = -7.19 \times 10^{-0.0110t} + 1.35 \times 10^{-0.107t} + 9.74$	+3.90
Potassium galacturonate	$^{\circ}S = -7.09 \times 10^{-0.0134t} + 1.12 \times 10^{-0.129t} + 9.91$	+3.94
Ammonium galacturonate	$^{\circ}S = -7.49 \times 10^{-0.0124t} + 0.80 \times 10^{-0.108t} + 9.99$	+3.30
Cadmium galacturonate	$^{\circ}S = -6.37 \times 10^{-0.0142t} + 1.09 \times 10^{-0.111t} + 9.90$	+4.62

^a 0.002 equivalent of the salt dissolved in 25 ml of water containing 0.002 equivalent of nitric acid and read in a 4-dm tube with a Bates saccharimeter. The volume after addition of the salt was 25.2 ml. The optical rotation is essentially that of the acid liberated from the salt.

$[\alpha]_D^{20} = ^{\circ}S \times 5.62$ (based on the weight of anhydrous galacturonic acid).

$^{\circ}S \times 0.3462 \times 25.2$

$[\alpha]_D^{20} = \frac{4 \times 0.002 \times \text{equivalent wt of the salt}}{4 \times 0.002 \times \text{equivalent wt of the salt}}$ (based on the weight of the salt).

^b The equations were calculated by the method described on page 156 of [18].

^c The initial rotation is the calculated value of $^{\circ}S$ when $t=0$.

^d 0.002 equivalent of the acid dissolved in 25 ml of water rather than in dilute nitric acid.

Equations for the mutarotations of α - and β -D-galacturonic acid, also given in table 1, were obtained by use of solutions containing 0.002 equivalent dissolved in 25 ml of water. The initial rotations at the right of the table are expressed in sugar degrees; multiplication by the factor 5.62 converts these values to specific rotation in terms of anhydrous galacturonic acid in the solution.

Inspection of the results reveals that the initial rotation of the acid set free from the calcium, strontium, sodium calcium, sodium strontium, sodium barium, sodium cadmium, sodium lead, and potassium calcium salts is in agreement with the initial rotation of α -D-galacturonic acid monohydrate, and that the initial rotation of the acid set free from the sodium, potassium, ammonium, and cadmium salts is in approximate agreement with the initial rotation of β -D-galacturonic acid. This is evidence that the salts in the first-mentioned group contain the alpha pyranose modification of galacturonic acid and that the salts in the second group contain the beta pyranose modification.⁴

This classification is supported further by the character of the changes in optical rotation which take place after dissolution of the salts. The change during the early part of the mutarotation of the first group of salts is more rapid than that during the later stages, and the mutarotation follows an equation of the type:

$$[\alpha]_t = A \times 10^{-m_1 t} + B \times 10^{-m_2 t} + C.$$

The net change during the early part of the mutarotation of the second group of salts is slow, and the mutarotation follows an equation of the type:

$$[\alpha]_t = -A' \times 10^{-m_1 t} + B' \times 10^{-m_2 t} + C.$$

The complex mutarotations of the first group are like the mutarotations characteristic of substances having the α -galacto-pyranose structure, whereas those of the second group are like the mutarotations characteristic of substances having the β -galacto-pyranose structure.

III. PREPARATION AND PROPERTIES OF SALTS OF GALACTURONIC ACID

1. SODIUM GALACTURONATE, $\text{NaC}_6\text{H}_9\text{O}_7$

This salt was prepared by neutralization of a 20-percent aqueous solution of galacturonic acid with sodium bicarbonate, followed by the addition of ethyl alcohol to the point of saturation. The crystals so obtained appear to differ from those described by Ehrlich and Schubert [8] in that they exhibit mutarotation and can be recrystallized from water. Ono [9] described a sodium salt crystallizable from water but failed to note any mutarotation. The material used in the present investigation was recrystallized from water by the addition of alcohol, and dried in a vacuum desiccator at room temperature over calcium chloride. Substantially quantitative yields were obtained.

Analysis: Calculated for $\text{NaC}_6\text{H}_9\text{O}_7$: C, 33.5; H, 4.2. Found: C, 33.5; H, 4.3.

⁴ Measurements were not made on the silver salt in the presence of nitric acid, but since the mutarotation in water is like that of salts having the beta pyranose structure, the silver salt is classified as a beta pyranose.

According to our measurements, in 4-percent aqueous solution, sodium galacturonate shows an initial specific rotation of $+11.5^\circ$, an equilibrium rotation of $+36.0^\circ$, and the mutarotation recorded in table 2. Previously, Ehrlich and Schubert [8] reported $[\alpha]_D^{25} = +36.02^\circ$ without mutarotation, and Ono [9] reported $[\alpha]_D^{20} = +38^\circ$, likewise without mutarotation. The initial and equilibrium rotations ($+11.5^\circ$ and $+36.0^\circ$) of the salt dissolved in water are considerably lower than the initial and equilibrium rotations of the salt dissolved in an equivalent quantity of aqueous nitric acid ($+19.7^\circ$ and $+49.2^\circ$). Similar differences have been found for other salts, and may be ascribed to the presence on carbon 5 of a carboxylate group in the water solutions and of a carboxyl group in the acid solutions.

The mutarotation of the salt (table 2) resembles the mutarotation of β -D-galacto-pyranose and other substances having the β -D-galacto-pyranose structure. The character of the changes shows that the sodium salt in aqueous solution establishes an equilibrium state involving at least three modifications. These must include the alpha and beta pyranose modifications and a furanose modification for the following reasons:

- (a) The substance crystallizes in the beta pyranose form.
- (b) Upon addition of a calcium salt, a sodium calcium salt of galacturonic acid containing the alpha pyranose modification crystallizes from solution.
- (c) The existence of a furanose modification in solution was shown by our previous observation [6] that a solution of sodium galacturonate on oxidation with bromine water gives rise to the optically active gamma and delta lactones of mucic acid. Presumably the gamma and delta lactones of mucic acid are formed directly from the furanose and pyranose modifications respectively.

The lactones of mucic acid just mentioned are obtained by oxidation of galacturonic acid and should not be confused with lactones of galacturonic acid formed by condensation of the carboxyl with the hydroxyl of carbon 2 or carbon 3. In dilute aqueous solutions of galacturonic acid, the concentrations of lactones are low, and their presence does not materially affect the optical rotations. Lactone formation does not occur in solutions of salts of galacturonic acid.

The mutarotation observed after dissolution of the sodium salt in nitric acid (table 3) resembles the mutarotation of β -D-galacturonic acid (table 4) at the same molecular concentration, but there are certain differences which indicate that the two samples were not of like purity. The sample of sodium galacturonate, when dissolved in an equivalent quantity of nitric acid, showed an initial rotation of $+3.90^\circ S$, a rapid mutarotation involving a change of $1.35^\circ S$, and a slow mutarotation involving a change of $7.19^\circ S$. The sample of galacturonic acid reported in table 4 showed an initial rotation of $+4.83^\circ S$, a rapid mutarotation reaction involving a change of $0.93^\circ S$, and a slow mutarotation reaction involving a change of $5.81^\circ S$. Other samples of β -D-galacturonic acid prepared by crystallization from both acetic acid and alcohol gave mutarotations which varied over a considerable range. It would therefore appear that the sample of β -D-galacturonic acid was not entirely free from the alpha modification, but unfortunately we have not been able to obtain a sample of galacturonic acid that has a lower initial rotation than that reported

here.⁵ The initial specific rotation of the acid set free from sodium galacturonate is $+21.9^\circ$, whereas for crystalline β -D-galacturonic acid Ehrlich and Schubert reported $+27^\circ$ [8], and we found $+31.1^\circ$ [6]. Since it is difficult to obtain the beta modification free from traces of the alpha, it is believed that the acid set free from the salt is more

TABLE 2.—Mutarotation of sodium galacturonate in water saturated with carbon dioxide ^a

4.0 g of NaC ₆ H ₇ O ₇ per 100 ml at 20° C, read in a 4-dm tube with a Bates saccharimeter.					
$^{\circ}S = -14.63 \times 10^{-0.0197t} + 3.45 \times 10^{-0.129t} + 16.42$.					
$[\alpha]_D^{20} = ^{\circ}S \times 2.19$.					
$[\alpha]_D^{20} = +11.5^\circ$ initially, $+36.0^\circ$ at equilibrium. ^b					
Time	Observed reading	$k_1 + k_2$	m_1	Deviation	m_2
Minutes	$^{\circ}S$				
1.9-----	+4.96			1.96	
3.1-----	+5.09	0.0041		1.38	0.127
5.7-----	+5.77	.0084		0.65	.126
10.5-----	+7.47	.0125		.14	.133
13.5-----	+8.55	.0141		.06	.131
16.6-----	+9.53	.0150			
22.8-----	+11.21	.0164	0.0196		
30.4-----	+12.72	.0172	.0196		
40.9-----	+14.14	.0180	.0198		
∞ -----	+16.42				
Average-----			0.0197		0.129

^a Mutarotation constants calculated by the method described on page 156 of [18].

^b The equilibrium value was carefully determined on a separate sample. The factor 2.19 is the ratio of the equilibrium specific rotation to the observed equilibrium rotation in $^{\circ}S$, or $36.0 \div 16.42$.

TABLE 3.—Mutarotation of sodium galacturonate dissolved in an equivalent quantity of aqueous nitric acid ^a

0.002 equivalent of NaC ₆ H ₇ O ₇ dissolved in 25 ml of 0.08 N aqueous nitric acid at 20° C, and read in a 4-dm tube. pH=2.4.					
$^{\circ}S = -7.19 \times 10^{-0.0110t} + 1.35 \times 10^{-0.107t} + 9.74$.					
$[\alpha]_D^{20} = ^{\circ}S \times 5.62$ (based on weight of anhydrous galacturonic acid).					
Time	Observed reading	m_1	Deviation	m_2	
Minutes	$^{\circ}S$				
2.6-----	+3.72		0.71		
3.7-----	+3.72		.52		0.123
4.8-----	+3.80		.42		.104
6.9-----	+3.98		.27		.098
8.8-----	+4.13		.14		.114
10.8-----	+4.39		.12		.094
16.1-----	+4.96				
19.7-----	+5.37	0.0108			
23.6-----	+5.80	.0112			
28.3-----	+6.23	.0110			
33.0-----	+6.64	.0111			
37.8-----	+6.99	.0111			
∞ -----	+9.74				
Average-----		0.0110			0.107

^a The values of m_1 and m_2 were calculated by the method described on page 156 of [18].

⁵ In this connection, it might be mentioned that the optical rotations of the crystalline modifications of galactose and arabinose also show wide variation, according to the manner in which the sugar is crystallized [19]

nearly a pure beta pyranose modification than any crystalline acid so far obtained. In view of the comparisons cited above, our crystalline sodium galacturonate is considered to be sodium β -D-galacturonate (sodium β -D-galacto-aldopentopyranose 5-carboxylate).

TABLE 4.—Mutarotation of β -D-galacturonic acid in water saturated with carbon dioxide

0.002 equivalent of β -D-galacturonic acid dissolved in 25 ml of water at 20° C, and read in a 4-dm tube. pH=2.4.				
$^{\circ}S = -5.81 \times 10^{-0.0120t} + 0.93 \times 10^{-0.092t} + 9.71.$				
$[\alpha]_D^{20} = ^{\circ}S \times 5.62.$				
Time	Observed reading	m_1	Deviation	m_2
<i>Minutes</i>	$^{\circ}S$			
1.9-----	+4.82		0.62	
3.8-----	+4.91		.43	0.084
5.1-----	+4.95		.28	.108
7.0-----	+5.15		.23	.084
8.9-----	+5.31		.14	.092
17.2-----	+6.11			
21.2-----	+6.49	0.0124		
24.9-----	+6.78	.0118		
30.1-----	+7.20	.0122		
39.2-----	+7.74	.0120		
53.6-----	+8.36	.0117		
70.1-----	+8.87	.0120		
∞ -----	+9.71			
Average-----		0.0120		0.092

2. POTASSIUM GALACTURONATE, $(K_6H_9O_7)_2 \cdot H_2O$

This salt was prepared by neutralization of an aqueous solution of galacturonic acid with an equivalent quantity of potassium carbonate. Crystallization was effected by adding methyl alcohol to the point of turbidity and allowing the solution to stand in a closed container. Additional methyl alcohol was added from time to time as crystallization proceeded. The crystals were separated and recrystallized from aqueous methyl alcohol and dried in a vacuum desiccator at room temperature over calcium chloride. The salt is more soluble in water than the sodium salt and crystallizes more slowly.

Analysis: Calculated for $K_2C_{12}H_{20}O_{15}$: C, 29.9; H, 4.2. Found: C, 29.7; H, 4.3.

In 4-percent aqueous solution, the salt shows a specific rotation of $+9.4^{\circ}$, (1.5 minutes after dissolution) $+31.6^{\circ}$ at equilibrium, and a complex mutarotation. The mutarotation which takes place when the salt is dissolved in an equivalent quantity of dilute nitric acid (equation given in table 1) resembles the mutarotation of β -D-galacturonic acid in water. The initial rotation and the course of the mutarotation show that the compound contains the beta pyranose modification and may be named potassium β -D-galacturonate, (potassium β -D-galacto-aldopentopyranose-5-carboxylate).

3. AMMONIUM GALACTURONATE, $(NH_4C_6H_9O_7)_2 \cdot H_2O$

A solution containing 5 g of galacturonic acid was neutralized with aqueous ammonium hydroxide, and the volume was adjusted to about 25 ml. Methyl alcohol was then added to saturation. The solution

was kept in a closed container for 2 days, and more alcohol was added as crystallization progressed. The crystals were separated, recrystallized from aqueous methyl alcohol, and, for analysis, dried in a vacuum desiccator at room temperature over calcium chloride.

Analysis: Calculated for $C_{12}H_{28}O_{15}N_2$: C, 32.7; H, 6.4. Found: C, 32.5; H, 6.5.

In 4-percent aqueous solution, the salt shows a specific rotation of $+10.2^\circ$ (1.7 minutes after dissolution), an equilibrium rotation of $+35.5^\circ$, and a complex mutarotation. The mutarotation in water is more rapid than that of either the sodium or the potassium salt. This fact may be explained by the catalytic effect of the ammonium ion. The mutarotation which takes place when the salt is dissolved in an equivalent quantity of dilute nitric acid (equation given in table 1) is slightly faster but resembles the mutarotation of β -D-galacturonic acid in water. Hence the compound contains the beta pyranose modification and may be designated ammonium β -D-galacturonate, (ammonium β -D-galacto-aldopentopyranose-5-carboxylate).

4. CADMIUM GALACTURONATE $Cd(C_6H_7O_7)_2 \cdot 2H_2O$

By mixing equivalent quantities of cadmium hydroxide and galacturonic acid in water a solution was obtained, which, on evaporation, gave crystalline cadmium galacturonate. The new salt crystallizes well, but it does not seem to be as characteristic of galacturonic acid as cadmium galactonate is of galactonic acid. It is considerably more soluble than the calcium salt and crystallizes more slowly. The material was recrystallized from aqueous ethyl alcohol and dried in a vacuum desiccator at room temperature over calcium chloride.

Analysis: Calculated for $CdC_{12}H_{22}O_{16}$: C, 27.0; H, 4.1. Found: C, 26.9; H, 4.2.

In 1.4-percent aqueous solution, the salt shows a specific rotation of $+13.9^\circ$ (1.9 minutes after dissolution), and an equilibrium rotation of $+28.4^\circ$. The mutarotation which takes place in water containing carbon dioxide is like that found for the alkali metal salts but is considerably more rapid. The mutarotation in nitric acid (equation given in table 1) resembles the mutarotation of β -D-galacturonic acid closely. Hence the salt contains the beta pyranose modification, and may be designated cadmium β -D-galacturonate.

5. SILVER GALACTURONATE, $(AgC_6H_7O_7)_2 \cdot H_2O$

Five grams of galacturonic acid monohydrate was dissolved in 5 ml of water and treated with an excess of freshly prepared silver carbonate. The mixture was allowed to stand for 15 minutes, filtered with the aid of a small quantity of decolorizing carbon, and the filtrate was placed in the refrigerator over-night. The crystals were separated, washed with ice water, and dried over calcium chloride at room temperature in a vacuum desiccator protected from light. The crystals are colorless platelets, which are sensitive to light and decompose in the course of several weeks.

Analysis: Calculated for $Ag_2C_{12}H_{20}O_{15}$: Ag, 34.8; C, 23.3; H, 3.3. Found: Ag, 34.7; C, 23.2; H, 3.3.

The sample used for the mutarotation measurements was crystallized from water in the absence of light, filtered, and used immediately without drying. The amount of salt in solution was calculated from

the silver content. In 3.2-percent aqueous solution, the salt shows a specific rotation of $+18.2^\circ$ (3.6 minutes after dissolution), an equilibrium rotation of $+25.1^\circ$, and a complex mutarotation similar to that of β -D-galacturonic acid. The initial rotation and the mutarotation indicate that the salt contains the beta pyranose modification.

6. CALCIUM GALACTURONATE $\text{Ca}(\text{C}_6\text{H}_9\text{O}_7)_2 \cdot \text{H}_2\text{O}$

(a) PREPARATION FROM GALACTURONIC ACID

Prior attempts to obtain a crystalline calcium galacturonate have been unsuccessful [9]. The difficulty in crystallizing salts of galacturonic acid may be ascribed at least in part to the existence in solution of the two pyranose modifications in dynamic equilibrium. We found that the sodium, potassium, ammonium, cadmium, and silver salts crystallize in the beta pyranose modification but were unable to obtain a similar calcium salt. However, a crystalline calcium salt of the alpha pyranose modification was obtained by adding a small quantity of water to a mixture of powdered calcium carbonate and α -D-galacturonic acid monohydrate in equivalent quantities. The mixture was rubbed with a glass rod and allowed to stand until crystallization took place. This material was used as seed for nucleation of calcium galacturonate sirups.

The sample used for analytical and optical rotation measurements was prepared by treating pure galacturonic acid in 10-percent aqueous solution with an excess of calcium carbonate, filtering the solution, and seeding with crystalline calcium galacturonate. When satisfactory crystallization had taken place, the crystals were separated, and the compound was recrystallized several times from hot water. It was finally dried in a vacuum desiccator over calcium chloride at room temperature.

Analysis: Calculated for $\text{CaC}_{12}\text{H}_{20}\text{O}_{15}$: Ca, 9.0; C, 32.4; H, 4.5. Found: Ca, 9.2; C, 32.2; H, 4.6.

TABLE 5.—Mutarotation of calcium galacturonate in water saturated with carbon dioxide

2.0 g of $\text{Ca}(\text{C}_6\text{H}_9\text{O}_7)_2 \cdot \text{H}_2\text{O}$ per 100 ml at 20°C , read in a 4-dm tube. $[\alpha]_D^{20} = ^\circ S \times 5.57$		
Time	Observed reading	$k_1 + k_2^a$
<i>Minutes</i>	$^\circ S$	
3.9	+13.47	0.081
4.5	+12.74	
5.0	+12.23	
6.3	+11.35	
7.6	+10.37	
9.0	+9.64	
10.4	+9.11	
12.4	+8.46	
15.3	+7.85	
18.4	+7.43	
22.3	+7.08	.063
26.3	+6.90	
31.1	+6.75	
∞	+6.61	

^a The decrease in the value of $k_1 + k_2$ shows that the mutarotation is complex. The rapid reaction was nearly complete at the time of the first reading.

At room temperature, calcium galacturonate crystallizes in the form of microscopic prisms, which build aggregates occluding considerable mother liquor; at slightly higher temperatures larger crystals separate and the mass is granular. Hence it is advantageous to effect the crystallization at slightly elevated temperatures. This can be accomplished readily in a distillation flask, or in a vacuum pan, held at about 40° C. The salt is soluble in about 10 parts of boiling water and crystallizes when the hot solution is cooled. At 20° C a saturated solution contains approximately 4.9 g of calcium galacturonate monohydrate per 100 ml. The salt is not appreciably soluble in alcohol or other organic solvents. Hence, crystallization can be conveniently effected by the addition of ethyl alcohol to an aqueous solution to the point of saturation, and the crystals can be washed, to advantage, with water containing about 15 percent of alcohol.

TABLE 6.—*Mutarotation of calcium galacturonate dissolved in an equivalent quantity of aqueous nitric acid*

0.002 equivalent of $\text{Ca}(\text{C}_6\text{H}_7\text{O}_7)_2 \cdot \text{H}_2\text{O}$ dissolved in 25 ml of 0.08 N aqueous nitric acid at 20° C, and read in a 4-dm tube. pH=2.2				
$^{\circ}S = +9.39 \times 10^{-0.0144t} + 2.25 \times 10^{-0.105t} + 9.93$ $[\alpha]_D^{20} = ^{\circ}S \times 5.62$ (based on weight of anhydrous galacturonic acid)				
Time	Observed reading	m_1	Deviation	m_2
<i>Minutes</i>	$^{\circ}S$			
2.3	+19.92	-----	1.29	-----
3.1	+19.50	-----	1.10	0.087
4.6	+18.70	-----	0.71	.113
5.9	+18.21	-----	.56	.101
7.3	+17.71	-----	.41	.100
9.7	+16.96	-----	.22	.122
14.9	+15.66	-----	-----	-----
20.0	+14.76	0.0146	-----	-----
25.6	+13.93	.0146	-----	-----
31.0	+13.30	.0143	-----	-----
37.1	+12.70	.0142	-----	-----
47.1	+11.89	.0145	-----	-----
∞	+9.93	-----	-----	-----
Average	-----	0.0144	-----	0.105

In 1.4-percent aqueous solution, calcium galacturonate shows a specific rotation of +75.0° (3.9 minutes after dissolution), an equilibrium rotation of +36.8°, and the complex mutarotation reported in table 5. A sample of calcium galacturonate dissolved in a chemically equivalent quantity of dilute nitric acid (table 6) showed an initial rotation of +21.6° *S*, a rapid mutarotation involving a change of 2.3° *S*, and a slow mutarotation involving a change of 9.4° *S*, whereas an aqueous solution of α -D-galacturonic acid (table 7) of like concentration showed an initial rotation of +21.6° *S*, a rapid change of 2.1° *S*, and a slow change of 9.5° *S*. The agreement shows that calcium galacturonate contains the alpha pyranose modification and may be designated calcium α -D-galacturonate.

(b) PREPARATION FROM CITRUS PECTIN

A mixture consisting of 1 kg of dry citrus pectin (210 grade, containing 84 percent of galacturonic acid by analysis) and 100 g of Pectinol 100D⁶ was added with stirring to 10 liters of water. The

⁶ A commercial pectinase manufactured by Rohm & Haas, Philadelphia, Pa.

TABLE 7.—Mutarotation of α -D-galacturonic acid in water saturated with carbon dioxide

0.002 equivalent of α -D-galacturonic acid dissolved in 25 ml of water at 20° C, and read in a 4-dm tube. pH=2.3				
$^{\circ}S = +9.52 \times 10^{-0.0119} + 2.08 \times 10^{-0.115} + 10.01$				
$[\alpha]_D^{20} = ^{\circ}S \times 5.62$ (based on weight of anhydrous galacturonic acid)				
Time	Observed reading	m_1	Deviation	m_2
<i>Minutes</i>	$^{\circ}S$			
2.2-----	+20.14	-----	1.16	-----
4.0-----	+19.24	-----	0.70	0.122
5.6-----	+18.66	-----	.48	.113
7.1-----	+18.18	-----	.33	.111
9.0-----	+17.64	-----	.19	.116
10.7-----	+17.24	-----	.13	.112
15.6-----	+16.22	-----	-----	-----
20.2-----	+15.45	0.0125	-----	-----
26.1-----	+14.70	.0116	-----	-----
30.6-----	+14.14	.0118	-----	-----
44.1-----	+12.89	.0117	-----	-----
∞ -----	+10.01	-----	-----	-----
Average....	-----	0.0119	-----	0.115

aqueous mixture was placed in an oven at 37° C for 2 days. During this period partial hydrolysis of the pectin took place, and the solution became highly acid and less viscous. The acidity was then adjusted to pH 3.9 by the addition of calcium carbonate (about 150 g), and the mixture was kept at 37° C for 5 more days. At this time, reduction values showed that the hydrolysis was substantially complete. The solution was heated to 80° C, neutralized with calcium carbonate, filtered, and concentrated in a vacuum still at about 40° C to a volume of 2 liters. During the evaporation considerable calcium galacturonate crystallized. The crystalline mixture was diluted with 500 ml of ethyl alcohol and allowed to stand over-night at 37° C. The crystals were separated by filtration, washed with aqueous alcohol, and recrystallized from 10 parts of hot water. The yield of pure calcium galacturonate (700 g) was 73 percent of the theoretical. Satisfactory results, but with somewhat lower yields, were obtained without the use of alcohol.

(c) CONVERSION TO GALACTURONIC ACID

A mixture consisting of 444 g of calcium galacturonate (1 mole) and 126 g of oxalic acid (1 mole) was added with stirring to 2 liters of hot water. The resulting calcium oxalate was separated by filtration and washed with hot water. The filtrate was concentrated to a sirup in a vacuum still at a temperature of 30° C. The sirup was seeded with α -D-galacturonic acid monohydrate, and evaporation was continued until the crystalline mixture in the distillation flask became thick. The crystals were separated by filtration and dried at room temperature. The first crop weighed 375 g, and additional crystalline galacturonic acid obtained by concentrating the mother liquor made the yield nearly quantitative.⁷ Under the conditions described, little or no decomposition takes place, but if during the evaporation the temperature is allowed to rise, the solution darkens, and the yield is less. Although crystallization from aqueous solution is convenient for large

⁷ Satisfactory results were obtained also by the use of sulfuric acid in place of oxalic acid. When sulfuric acid is used, an excess must be carefully avoided.

quantities, crystallization from aqueous alcohol, or aqueous acetic acid, is preferable for small quantities, because there is less loss in handling the material.

7. STRONTIUM GALACTURONATE, $\text{Sr}(\text{C}_6\text{H}_7\text{O}_7)_2 \cdot 5\text{H}_2\text{O}$

Crystals of strontium galacturonate were first obtained by the addition of a small amount of water to a finely powdered mixture of equivalent quantities of α -D-galacturonic acid and strontium carbonate. The seed crystals thus obtained were used in subsequent preparations. The salt was prepared in quantity by neutralizing a 10-percent solution of galacturonic acid in hot water with a strontium carbonate, filtering, and adding ethyl alcohol to saturation. The solution was allowed to cool slowly, since the crystals so obtained are larger and have better filtering properties than those formed from concentrated aqueous solution or by the addition of alcohol to a solution at room temperature. The compound was recrystallized from aqueous alcohol, separated, and dried in a vacuum desiccator at room temperature over calcium chloride. At 20° C a saturated aqueous solution of strontium galacturonate pentahydrate contains 3.0 g per 100 ml of solution.

Analysis: Calculated for $\text{SrC}_{12}\text{H}_{28}\text{O}_{19}$: C, 25.6; H, 5.0. Found: C, 25.8; H, 5.0.

In 1.4-percent aqueous solution, strontium galacturonate shows a specific rotation of +63.1° (2.7 minutes after dissolution), an equilibrium rotation of +29.1°, and a complex mutarotation. A sample containing 0.002 equivalent of strontium galacturonate, when dissolved in 25 ml of 0.08 N nitric acid, showed an initial rotation of +21.7° S, a rapid mutarotation involving a change of 2.4° S, and a slow mutarotation involving a change of 9.3° S (equation given in table 1). These values are in substantial agreement with the values obtained from similar measurements with α -D-galacturonic acid. Hence the new salt may be designated strontium α -D-galacturonate.

8. SODIUM CALCIUM GALACTURONATE, $\text{NaCa}(\text{C}_6\text{H}_7\text{O}_7)_3 \cdot 6\text{H}_2\text{O}$

(a) PREPARATION FROM GALACTURONIC ACID

This new crystalline salt (see footnote 3, page 78) was prepared by treating a solution containing 3 equivalents of galacturonic acid with 1 equivalent of sodium hydroxide and an excess of calcium carbonate. The mixture was filtered and concentrated under reduced pressure until crystallization took place. For analysis the salt was recrystallized from hot water, and dried in a vacuum desiccator at room temperature over calcium chloride. The yield of the double salt was substantially quantitative.

The salt crystallizes readily from hot water, in which it is soluble to the extent of approximately 15 g per 100 ml. At 20° C the solubility in water is only 1.8 g per 100 ml of solution. The facility with which it crystallizes, its low solubility, and other desirable properties make the compound of unusual importance for the separation of galacturonic acid.

Analysis: Calculated for $\text{NaCaC}_{18}\text{H}_{39}\text{O}_{27}$: Ca, 5.3; C, 28.8; H, 5.2. Found: Ca, 5.4; C, 28.8; H, 5.2.

The salt might be composed of alpha galacturonate radicals, of beta galacturonate radicals, or of alpha and beta galacturonate radicals in

the proportions of 1:2 or 2:1. In 1.4-percent aqueous solution it shows a specific rotation of $+61.7^\circ$ (3.4 minutes after dissolution), an equilibrium rotation of $+32.4^\circ$, and a complex mutarotation. A sample of sodium calcium galacturonate containing 0.002 equivalent when dissolved in 25 ml of 0.08 normal nitric acid showed an initial rotation of $+21.9^\circ\text{S}$, a rapid mutarotation involving a change of 2.5°S , and a slow change of 9.3°S , whereas a sample of α -D-galacturonic acid of like concentration showed an initial rotation of $+21.7^\circ\text{S}$, a rapid mutarotation involving a change of 2.1°S , and a slow change of 9.5°S (equation given in table 1). The agreement of the mutarotation of the acidified salt with that of α -D-galacturonic acid shows that the crystalline salt contains only the alpha pyranose modification of the acid.

(b) PREPARATION FROM PECTIC ACID⁸

Sodium calcium galacturonate is particularly useful for separating galacturonic acid from the hydrolytic liquors of plant materials. The process described here involves enzymatic hydrolysis of a mixture of pectic acid and sodium pectate, followed by neutralization of the hydrolyzate with calcium carbonate and crystallization of the resulting sodium calcium galacturonate. The procedure, which is described in considerable detail, is suitable for the production of either large or small quantities of the salt.

Dry pectic acid and sodium bicarbonate were mixed in such proportion⁹ that the acidity of the mixture in 7 parts of water was between pH 3.8 and 4.0. One kilogram of dry sodium bicarbonate, pectic acid mixture was added in portions with stirring to 7 liters of water. The carbon dioxide liberated caused considerable foaming, which was kept under control by the addition of an antifoam agent (hexyl alcohol). Fifty grams of Pectinol 100D (see footnote 6, page 87) and sufficient toluene to prevent mold growth were added, and the mixture was allowed to stand at 37°C until hydrolysis was complete, (about 8 days). The material was then heated to about 80°C and neutralized with calcium carbonate. About 50 g of calcium carbonate was required. After the addition of 150 g of calcium nitrate,¹⁰ $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, the mixture was heated to boiling and filtered with the aid of 25 g of decolorizing carbon and 25 g of infusorial earth. The residue on the filter was washed with 3 liters of hot water containing 25 g of calcium nitrate.

The filtered solution was evaporated¹¹ under reduced pressure at a temperature below 50°C . Crystallization of sodium calcium galacturonate took place as evaporation proceeded; the process was interrupted and the crystals were separated when the mixture of crystals and sirup reached a convenient consistency. Additional material was obtained by evaporation of the mother liquor. The yield of relatively pure crystalline sodium calcium galacturonate was approximately 750 g, or 85 percent of the galacturonic acid content of the

⁸ The product was supplied by the California Fruit Growers' Exchange, Ontario, Calif.

⁹ Usually about 1 part of sodium bicarbonate is required for 4 to 5 parts of pectic acid, but the amount varies for different lots. The proportion for each batch of pectic acid may be ascertained by mixing 5-g samples with various amounts of sodium bicarbonate and determining the pH of the mixture in 35 ml of water. When this proportion has been ascertained for the particular pectic acid employed, the trial adjustment is unnecessary in subsequent preparations, but the pH of the mixture to be hydrolyzed should always be checked.

¹⁰ The addition of calcium nitrate at this point causes coagulation of the colloidal material and greatly facilitates filtration. Calcium nitrate is necessary in the wash water to prevent peptization of the residue. The total amount of calcium ion added must be sufficient for the formation of the double salt.

¹¹ A substantial crop of crystalline sodium calcium galacturonate may be obtained without evaporation if the liquid is cooled, seeded, and allowed to stand.

pectic acid used. Analyses of three samples of commercial pectic acid by the carbon dioxide method showed the presence of galacturonic acid corresponding to 85, 90, and 95 percent of the pectic acid. In the example reported above, the pectic acid having the lowest galacturonic acid content was used. Higher yields were obtained with the other samples.

(c) CONVERSION TO SODIUM GALACTURONATE

A mixture consisting of 0.5 mole (375.3 g) of dry sodium calcium galacturonate and 0.5 mole (67 g) of sodium oxalate was added in small portions with stirring to 2 liters of hot water. The resulting calcium oxalate was separated by filtration. The filtrate was concentrated under reduced pressure at 45° C to a thin sirup, which was saturated with ethyl alcohol and seeded with crystalline sodium galacturonate. When crystallization was substantially complete, the crystals were separated by filtration and washed with aqueous alcohol. The first crop weighed 310 g. Additional crystals obtained by concentrating the mother liquor made the yield substantially quantitative.

(d) CONVERSION TO GALACTURONIC ACID

One mole (750.6 g) of sodium calcium galacturonate was mixed with exactly 1,500 ml of 2 *N* aqueous sulfuric acid, and the resulting calcium sulfate was separated by filtration. The solution was concentrated at 30° C under reduced pressure to a volume of about 800 ml, and 200 ml of 50-percent aqueous acetic acid and seed crystals of galacturonic acid hydrate were added. Crystallization was allowed to take place under constant stirring at room temperature. The crystals were collected on a filter and washed with aqueous acetic acid. The first crop (440 g) $[\alpha]_D^{25} = +51.8^\circ$, was relatively pure galacturonic acid hydrate. By concentrating the mother liquor, additional crops of 60 g, $[\alpha]_D^{25} = +48.0^\circ$, and 20 g, $[\alpha]_D = +48.5^\circ$, were obtained. The total, 520 g, corresponds to 82 percent of the theoretical yield.

9. SODIUM STRONTIUM GALACTURONATE, $\text{NaSr}(\text{C}_6\text{H}_7\text{O}_7)_3 \cdot 6\text{H}_2\text{O}$

This salt was prepared by neutralizing a solution containing 2 equivalents of α -*D*-galacturonic acid with strontium carbonate, and combining this with a solution containing 1 equivalent of sodium galacturonate. The salt separates readily and can be recrystallized from about 7 parts of hot water. At 20° C it is soluble only to the extent of 1.6 g per 100 ml. For analysis the recrystallized salt was dried over calcium chloride at room temperature in a vacuum desiccator.

Analysis: Calculated for $\text{NaSrC}_{18}\text{H}_{39}\text{O}_{27}$: Sr, 11.0; C, 27.1; H, 4.9. Found: Sr, 11.0; C, 26.9; H, 4.8.

In 1.4-percent aqueous solution, sodium strontium galacturonate shows a specific rotation of +48.3° (4.0 minutes after dissolution), an equilibrium rotation of +30.2°, and a complex mutarotation. The mutarotation which takes place when the compound is dissolved in an equivalent quantity of dilute nitric acid (table 1) follows substantially the same equation as the mutarotation of α -*D*-galacturonic acid in water. The initial rotation and the course of the mutarotation show that the crystalline compound contains the alpha pyranose modification of galacturonic acid.

10. SODIUM BARIUM GALACTURONATE, $\text{NaBa}(\text{C}_6\text{H}_7\text{O}_7)_3 \cdot 6\text{H}_2\text{O}$

A mixture consisting of 25 g of sodium calcium galacturonate and 4.2 g of powdered oxalic acid was added in portions to 40 ml of hot water. After several minutes, 7 g of barium carbonate was added and when reaction was complete the mixture was filtered. The filtered solution was placed in the refrigerator. In the course of 1 day, crystalline sodium barium galacturonate separated in good yield. The product was recrystallized from a minimum amount of hot water and for analysis dried in a vacuum desiccator at room temperature over calcium chloride.

Analysis: Calculated for $\text{NaBaC}_{18}\text{H}_{39}\text{O}_{27}$: C, 25.5; H, 4.6. Found: C, 25.5; H, 4.8.

In 1.4-percent aqueous solution, sodium barium galacturonate shows a specific rotation of $+57.2^\circ$ (3.9 minutes after dissolution), an equilibrium rotation of $+27.8^\circ$, and a complex mutarotation. The mutarotation which takes place when the compound is dissolved in an equivalent quantity of dilute nitric acid (table 1) shows that the crystalline substance contains the alpha pyranose modification of galacturonic acid.

11. SODIUM CADMIUM GALACTURONATE, $\text{NaCd}(\text{C}_6\text{H}_7\text{O}_7)_3 \cdot 6\text{H}_2\text{O}$

This salt was prepared by neutralizing a solution containing 2 equivalents of *D*-galacturonic acid with cadmium hydroxide, and combining this with a solution containing 1 equivalent of sodium galacturonate. The solution was filtered and evaporated to a thin sirup, from which the crystalline salt separated in the course of a day. The salt was recrystallized by dissolving it in a small quantity of water, and adding ethyl alcohol to the point of saturation. The crystals that separated were collected on a filter, washed with aqueous alcohol, and dried in a vacuum desiccator at room temperature over calcium chloride.

Analysis: Calculated for $\text{NaCdC}_{18}\text{H}_{39}\text{O}_{27}$: C, 26.3; H, 4.8. Found: C, 26.6; H, 4.9.

In 1.4-percent aqueous solution, sodium cadmium galacturonate shows a specific rotation of $+53.3^\circ$ (2.1 minutes after dissolution), an equilibrium rotation of $+27.3^\circ$, and a complex mutarotation. The mutarotation which takes place when the compound is dissolved in an equivalent quantity of dilute nitric acid shows that the crystalline substance contains the alpha pyranose modification of galacturonic acid. The mutarotation data for the substance in an equivalent quantity of nitric acid is given in the form of an equation in table 1.

12. SODIUM LEAD GALACTURONATE, $\text{NaPb}(\text{C}_6\text{H}_7\text{O}_7)_3 \cdot 6\text{H}_2\text{O}$

A mixture of 30 g finely powdered sodium calcium galacturonate and 5.5 g of oxalic acid was added to 45 ml of water. The mixture was stirred for 15 minutes, after which an excess of freshly prepared normal lead carbonate was added, and stirring was continued for 15 minutes. Then the mixture was filtered with the aid of decolorizing carbon, and the filtrate was allowed to stand in the refrigerator overnight. The crystalline sodium lead galacturonate which formed was

separated by filtration and washed with aqueous ethyl alcohol (7 parts of water to 1 part of alcohol). The product was recrystallized from water and dried in a vacuum desiccator over calcium chloride at room temperature. Sodium lead galacturonate crystallizes from fairly concentrated aqueous solutions; it is necessary to avoid overheating, since decomposition of the salt in solution takes place readily.

Analysis: Calculated for $\text{NaPbC}_{18}\text{H}_{39}\text{O}_{27}$: C, 23.6; H, 4.3. Found: C, 23.6; H, 4.2

In 1.4-percent aqueous solution, sodium lead galacturonate gives an equilibrium specific rotation of $+29.0^\circ$. Presumably because of the catalytic action of the lead ion the mutarotation is too rapid to be measured. In the presence of dilute nitric acid, the mutarotation reaction (table 1) is more rapid than that of the other double salts reported here, but it is undoubtedly of like character. Hence it is concluded that the crystalline sodium lead salt contains the alpha pyranose modification of galacturonic acid.

13. POTASSIUM CALCIUM GALACTURONATE, $\text{KCa}(\text{C}_6\text{H}_7\text{O}_7)_3 \cdot 6\text{H}_2\text{O}$

Ten grams of galacturonic acid monohydrate was mixed with 1.09 g of potassium carbonate in 50 ml of water. Calcium carbonate was then added, and after a few minutes the excess was removed by filtration. The solution was saturated with ethyl alcohol and brought to crystallization by scratching the walls of the container with a glass rod. The crystalline material was separated and recrystallized by dissolving in water at room temperature, and adding alcohol. If alcohol is added to a warm, aqueous solution, normal calcium galacturonate will crystallize in place of the double salt. For analysis the recrystallized potassium calcium galacturonate was dried in a vacuum desiccator at room temperature over calcium chloride.

Analysis: Calculated for $\text{KCaC}_{18}\text{H}_{39}\text{O}_{27}$: Ca, 5.2; C, 28.2; H, 5.1. Found: Ca, 5.3; C, 28.2; H, 5.1.

In 1.4-percent aqueous solution the salt shows a specific rotation of $+69.2^\circ$ (1.6 minutes after dissolution), an equilibrium rotation of $+31.4^\circ$, and a complex mutarotation. The mutarotation which takes place when the salt is dissolved in an equivalent quantity of dilute nitric acid is similar to that of α -D-galacturonic acid in water and follows nearly the same equation (table 1). Hence the double salt is a derivative of the alpha pyranose modification of crystalline galacturonic acid.

IV. SUMMARY

The salts listed in table 8 have been prepared and their properties studied. With the exception of the sodium salt, all the compounds are new crystalline substances. The sodium salt reported here contains the beta pyranose modification and appears to differ from that previously reported in that it exhibits mutarotation. A unique class of double salts containing a monovalent and a divalent metal in combination with three alpha galacturonate radicals was discovered, and the use of sodium calcium galacturonate and of calcium galacturonate for the preparation of galacturonic acid from pectic substances was described.

TABLE 8.—Salts of galacturonic acid

Salt	Optical rotation ^a [α] _D ²⁰	C ^b	Modification of acid present
NaC ₆ H ₅ O ₇	+36.0	4	Beta pyranose.
(KC ₆ H ₅ O ₇) ₂ ·H ₂ O.....	+31.6	4	Do.
(NH ₄ C ₆ H ₅ O ₇) ₃ ·H ₂ O.....	+35.5	4	Do.
Cd(C ₆ H ₅ O ₇) ₂ ·2H ₂ O.....	+28.4	1.4	Do.
(AgC ₆ H ₅ O ₇) ₂ ·H ₂ O.....	+25.1	3.2	Do.
Ca(C ₆ H ₅ O ₇) ₂ ·H ₂ O.....	+36.8	1.4	Alpha pyranose.
Sr(C ₆ H ₅ O ₇) ₂ ·5H ₂ O.....	+29.1	1.4	Do.
NaCa(C ₆ H ₅ O ₇) ₃ ·6H ₂ O.....	+32.4	1.4	Do.
NaSr(C ₆ H ₅ O ₇) ₃ ·6H ₂ O.....	+30.2	1.4	Do.
NaBa(C ₆ H ₅ O ₇) ₃ ·6H ₂ O.....	+27.8	1.4	Do.
NaCd(C ₆ H ₅ O ₇) ₃ ·6H ₂ O.....	+27.3	1.4	Do.
NaPb(C ₆ H ₅ O ₇) ₃ ·6H ₂ O.....	+29.0	1.4	Do.
KCa(C ₆ H ₅ O ₇) ₃ ·6H ₂ O.....	+31.4	1.4	Do.

^a At equilibrium in water.^b Concentration of salt in grams per 100 ml of aqueous solution.

• See footnote 3, page 78.

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